

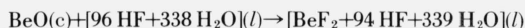
Enthalpies of Solution of BeO(c) in HF(aq) and in HCl(aq)*

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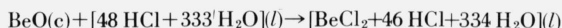
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An adiabatic solution calorimeter was used to measure the enthalpies of the following reactions:



$$\Delta H \text{ at } 298.15 \text{ K} = -101.30 \pm 0.20 \text{ kJ} \cdot \text{mol}^{-1}$$



$$\Delta H \text{ at } 352.58 \text{ K} = -54.19 \pm 0.22 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta H \text{ at } 298.15 \text{ K} = -53.0 \pm 2.0 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta C_p \text{ is } 12.5 \pm 2.8 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \text{ for the first reaction in the range } 298 \text{ to } 325 \text{ K.}$$

Key words: BeO(c), enthalpy of soln in HF(aq); BeO(c), enthalpy of soln in HCl(aq); BeO(c), enthalpy of reaction in HF(aq); beryllium oxide; enthalpy of solution; heat of solution; thermochemistry.

1. Introduction

The value for the enthalpy of formation of beryllium oxide is an important quantity in establishing values for the enthalpies of formation of many other beryllium compounds. Determination of this quantity by direct combustion has been subject to considerable uncertainty, as have the various indirect methods [1].¹ A precision adiabatic solution calorimeter, designed to measure the energy changes in slow reactions, was employed to determine the enthalpies of solution of BeO(c) in both aqueous hydrofluoric and hydrochloric acids as functions of temperature and acid concentration. Effectively complete reaction was obtained in all cases. These values were combined with other data by Parker [1] to obtain a more reliable value for the enthalpy of formation of BeO(c).

2. Sample and Calorimetric Solutions

2.1. BeO(c)

The crystalline beryllium oxide was obtained from the Brush Beryllium Company,² Elmore, Ohio. It was identified as UOX grade, -325 mesh. The certificate of analysis supplied with the material indicated 0.33

percent loss on ignition, 0.31 percent loss on drying, 0.23 percent SO₃ and a total of less than 280 ppm of metallic elements identified in spectroscopic analysis. The principal impurities were 50 ppm Al, 15 ppm Fe, 40 ppm Mg, 50 ppm Na, 30 ppm Ca, 50 ppm Si, and <20 ppm Zn. We confirmed the loss on drying at ~540 K, the spectroscopic analysis³ was confirmed, and the crystallinity of the sample was confirmed by x-ray powder diffraction analysis.⁴

The 1.0-g or 0.3-g samples for the calorimetric experiments were dried overnight at approximately 540 K and stored in a desiccator until they were transferred in a dry box to the weighed sample holder. The determination of the sample mass is estimated to be accurate to ± 0.03 mg.

A slight inhomogeneity in the BeO sample became apparent when traces of undissolved residues were found in the final HCl solutions. There were two types of "undissolved" residue: a very finely divided material which was present at low reaction temperatures and in preliminary experiments of short duration, and coarser particles with diameters of the order of 1 mm which under the microscope appeared to be clusters of crystals. The finely divided material was identified as unreacted BeO by x-ray powder diffraction.⁴ The coarser material definitely contributed additional lines to the BeO pattern, but the composition was not identified. Spectroscopic analysis of the material indicated

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¹ Figures in brackets indicate literature references at the end of this paper.

² Certain commercial material is identified in this paper in order to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by the National Bureau of Standards.

³ Performed by V. C. Stewart, Spectrochemical Analysis Section, Analytical Chemistry Division.

⁴ Performed by H. E. Swanson, Crystallography Section, Inorganic Materials Division.

Be as the major constituent with Al and Si as minor constituents, and it was concluded that this coarser material which was insoluble in the HCl solutions even at 363 K was probably mixed oxides of Be, Al, and Si. Further identification of the insoluble residue was not attempted in view of the very small quantities which were not homogeneously distributed in the calorimetric samples. Various final calorimetric solutions contained from zero to five of the "insoluble" particles.

In the hydrofluoric acid calorimetric solutions, solution of the BeO sample appeared to be complete and no undissolved residue was visible.

2.2. Calorimetric Solutions of Aqueous Hydrofluoric Acid

The calorimetric solutions were portions of seven stock solutions prepared by dilution of ACS reagent-grade concentrated hydrofluoric acid (48–51%) with distilled water. The stock solutions were analyzed by titration of weighed samples, 3 to 5 g, with 0.918 *N* standard sodium hydroxide solution using phenolphthalein as an indicator.

The calorimetric solutions were clear after the reactions, with no undissolved residue visible. Analysis of the final solutions was not attempted and the products were assumed to be BeF₂ and H₂O in solution. Soda lime (containing a color indicator) was found to be useful in safely neutralizing the HF solutions from the calorimetric experiments. The neutralization was done in an ice bath with stirring to prevent excessive heating.

2.3. Calorimetric Solutions of Aqueous Hydrochloric Acid

The calorimetric solutions were portions of four stock solutions prepared by dilution of cp reagent-grade concentrated hydrochloric acid (37–38%) with distilled water. The stock solutions were analyzed by titration using anhydrous sodium carbonate prepared from reagent-grade sodium carbonate dried at 543 K for 1 h; bromophenol blue was the indicator.

The final calorimetric solutions were not analyzed and the products were assumed to be BeCl₂ and H₂O in solution.

3. Units, Physical Constants, and Calibrations

The masses of samples given in the following tables were obtained using a buoyancy factor calculated from the density, 3.03 g · cm⁻³ [2], for BeO(c).

Values for atomic weights were taken from the 1969 Table of Atomic Weights [3]. Molecular weights used are as follows: BeO, 25.01158; HF, 20.0064; HCl, 36.461; and H₂O, 18.0154.

The unit of energy is the joule (J) and 1 thermochemical calorie = 4.1840 J.

Electrical energy measurements were based on the values of a saturated Weston standard cell last calibrated in April 1968, and of standard resistors last calibrated in October 1966. Temperature measurements are based on the 25-Ω platinum resistance

thermometer calibration of 1961.⁵ These are all NBS certified calibrations. The history of calibrations of this equipment provided confidence in the values at the actual time of these experiments because of the consistent trend in the calibrated values over the years. The measurements reported in this paper were made between March 1967 and November 1968.

4. Calorimeter and Procedures

The high precision adiabatic solution calorimeter used for these measurements is described in detail by Prosen and Kilday [4]. In this work, the largest cylinder (volume 2.7 cm³) was used in the sample holder to avoid the necessity for packing the very finely divided sample. In a dry box, the BeO sample was added to the cylinder shown at the top of figure 1 and the sample holder was assembled as shown at the bottom before weighing.

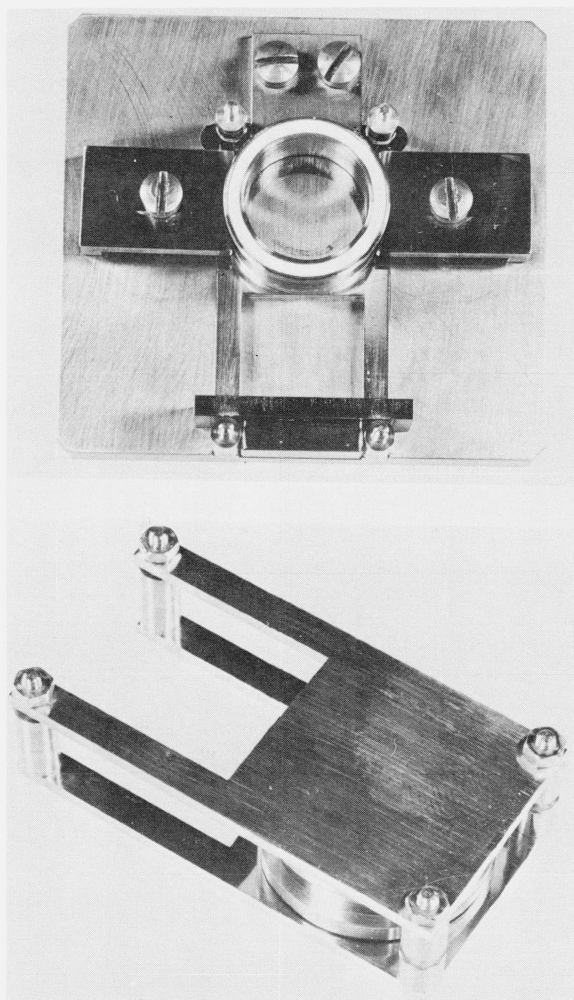


FIGURE 1. (upper) The sample holder in a clamp ready for filling, and (lower) the assembled sample holder ready for weighing.

⁵ See [4] for thermometer calibration data. On this thermometer, one kelvin is 0.10104 Ω at 298.15 K and 0.09939 Ω at 353.15 K.

The time required for one complete experiment varied from approximately 8 h for the BeO in HF(aq) to 4 days for the BeO in HCl(aq). The duration of the chemical reaction period varied with the concentration of the solvent, the temperature of reaction, and the stirring rate. The four reaction periods plotted in figure 2 show the variations from 1 h to 4.5 h for solutions of BeO(c) in HF(aq). They represent various concentrations of HF(aq) at 298 K and 323 K and a stirring rate of 250 rpm. This stirring rate was used for all of the BeO solutions in HF(aq) except as noted.

The solutions of BeO(c) in HCl(aq) were made with a stirring rate of 350 rpm but only in the first experiment was there continuous stirring during the 20-h reaction period. In all other experiments the stirrer and the thermometer current were turned off for 17.5 h during the chemical reaction. A drift rate for the unstirred system (discussed in sec. 5.3) was measured at the beginning and the end of these experiments. The observed heat loss was assumed to be due to evaporation through the stirrer tube for which approximate corrections were applied. During the stirred portions of the experiments, evaporative heat losses were included in the slopes of the rating periods. The calibrations of

the initial and final systems compensate for changes in the heat capacity of the system.

The point at which the reactions were completed was not clearly defined, especially in the very slow reactions, but this is not critical since the calorimeter operates under adiabatic conditions. A reaction was usually assumed to be complete when the slope of the temperature curve was approximately the same as that of the initial rating period, or when the slope of the final time-temperature curve had not changed significantly for 1 h. Although these conditions were met after 8 h in the solution of BeO(c) in HCl(aq) at 358 K, more than 1 percent of the sample remained undissolved in the final solution. When the reaction time was extended overnight, the undissolved sample in the final solution was negligible.

In the solutions of BeO in HF(aq) at 313 and at 323 K, the temperature of the shield lagged behind that of the vessel for several minutes after starting the reaction. Small corrections were calculated for these experiments based on a previously determined value for the heat leak constant, $k = 3.0 \times 10^{-3} \text{ min}^{-1}$ [4]. The largest of these corrections (Expts. No. 28 and 30) was 0.09 percent of the corrected temperature

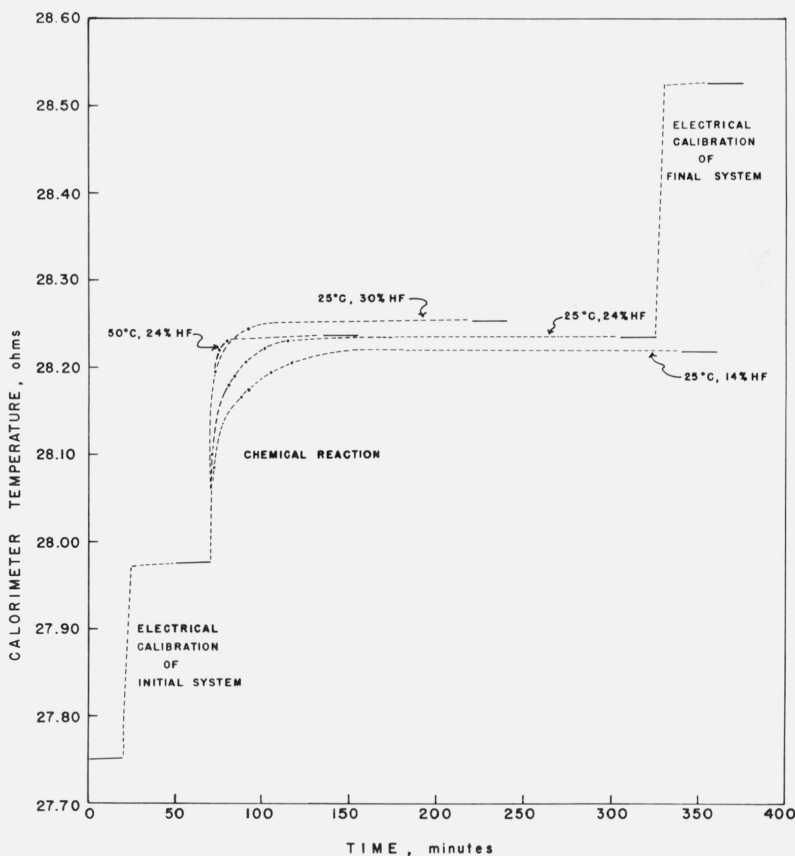


FIGURE 2. Time-temperature curves for experiments in which samples of BeO(c) were dissolved in HF(aq) under various conditions.

The solid lines are rating periods and the dashed lines are reaction or electrical calibration periods. The electrical calibration curves are shown for only one experiment.

rise, ΔR_c . The area, $182 \mu\text{V} \cdot \text{min}$, was obtained from the record of the difference between the temperatures of the calorimeter vessel and of the adiabatic shield. The six-junction control thermocouples produce $240 \mu\text{V} \cdot \text{K}^{-1}$ and the thermal coefficient of the resistance thermometer is $10 \text{ K} \cdot \Omega^{-1}$. The correction, $230 \mu\Omega$, in a total temperature rise of 0.254Ω is 0.09 percent.

The final calorimeter solutions were not analyzed except by weighing the amounts of undissolved residues in the HCl solutions. The final solutions were allowed to stand at least 1 h after which approximately 250 cm^3 of the solution was siphoned off (to avoid disturbing the solid particles which had settled to the bottom of the vessel). The remaining solution was diluted to approximately 300 cm^3 with distilled water and allowed to stand at least 1 h. Approximately 280 cm^3 of the solution again was siphoned off. The larger "insoluble" particles were removed with a spatula and the finely divided residue was transferred with the solution to a weighed platinum crucible by means of a dropper. The solution was evaporated and the residue was dried for 2 h at 543 K , cooled, and weighed. The mass of the residue was subtracted from the sample mass to give the mass of sample reacted.

5. Experimental Results

5.1. Solution of BeO(c) in HF(aq)

The enthalpies of solution of crystalline beryllium oxide in aqueous hydrofluoric acid solutions were measured in 29 experiments at reaction temperatures ranging from 293 K to 325 K and in 14 to 30 wt percent HF(aq). Most of the BeO samples weighed about 1 g. However, 0.3-g samples were used for the reactions at 293 K in order to obtain the desired mean temperature of reaction with a starting temperature of 291 K , the lower limit of the controlled room temperature. At 298 K , 0.3-g samples were also used in three experiments for comparison with those at 293 K . Unfortunately the use of these small samples resulted in a large reduction in the precision of the measurements because of the smaller temperature rise, and the results were not used in the determination of ΔC_p for the reaction. However, they were useful in showing that a change in the ratio of the Be to HF at this concentration has little effect on the enthalpy of solution.

Tables 1 and 2 give the data for the 29 experiments in which the enthalpy of solution of BeO(c) in HF(aq)

TABLE 1. Composition of reactants in the calorimetric systems for solutions of BeO(c) in HF(aq)

Expt. No.	Initial composition			Conc. of HF soln.	Mass of HF soln.
	BeO	HF	H ₂ O		
	<i>mol</i>	<i>mol</i>	<i>mol</i>	<i>wt %</i>	<i>g</i>
1	0.040166	3.648	12.737	24.13	302.45
2	.039940	3.858	13.326	24.33	317.27
3	.039247	3.826	13.359	24.13	317.21
4	.039186	3.859	13.327	24.33	317.29
5	.035230	3.859	13.328	24.33	317.30
6	.039722	3.117	14.146	19.66	317.20
7	.040649	3.140	14.121	19.80	317.21
8	.040709	3.119	14.152	19.66	317.34
9	.039771	3.826	13.358	24.13	317.18
10	.040045	3.825	13.356	24.13	317.14
11	.013265	3.140	14.122	19.80	317.23
12	.013035	3.117	14.145	19.66	317.18
13	.013414	3.140	14.122	19.80	317.23
14	.039897	2.228	15.139	14.05	317.31
15	.038740	2.227	15.129	14.05	317.12
16	.039486	2.228	15.135	14.05	317.23
17	.012077	3.119	14.152	19.66	317.35
18	.012561	3.140	14.125	19.80	317.29
19	.012302	3.118	14.151	19.66	317.31
20	.041156	4.716	12.361	29.76	317.03
22	.039519	4.719	12.370	29.76	317.27
23	.041010	4.721	12.374	29.76	317.37
24	.040988	4.720	12.372	29.76	317.31
25	.040436	3.844	13.348	24.23	317.36
26	.038455	3.844	13.351	24.23	317.43
27	.039967	3.844	13.348	24.23	317.37
28	.041170	3.843	13.348	24.23	317.35
29	.033059	3.842	13.344	24.23	317.27
30	.040682	3.843	13.347	24.23	317.34

was measured. In this and in subsequent tables, EEE_i and EEE_f are the electrical energy equivalents of the initial and final systems. The methods for calculating the electrical energy equivalents; the stirring energy corrections; the corrected temperature rise, ΔR_c ; and the mean temperature of reaction, \bar{T} , were described previously [4]. The enthalpy of solution at the temperature of reaction, which we define as the mean temperature of reaction, was calculated using the following equation:

$$-\Delta H(T) = \{ [1/2(EEE_i + EEE_f)] (\Delta R_c) \} / \text{(moles of sample)}.$$

Expt. No. 21 was lost because of a problem with the adiabatic controls and the results are not included in the tables.

A least squares fit of the data from the 13 experiments using 24 percent HF (Nos. 1, 2, 3, 4, 5, 9, 10, 25, 26, 27, 28, 29, and 30) given in table 2 resulted in the following equation for the relationship of temperature (in K) and the enthalpy of solution (in $\text{kJ} \cdot \text{mol}^{-1}$) of BeO(c) in 24 percent HF:

$$\Delta H \text{ at } T = -101.20^* + 0.0125 (T - 298.15 \text{ K}).$$

Thus, ΔC_p for the reaction is $+12.5 \pm 2.8 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ (or $+2.99 \pm 0.69 \text{ cal} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$) in the range 298 K to 324 K. The standard error of the estimate of ΔH is $\pm 0.11 \text{ kJ} \cdot \text{mol}^{-1}$ and of the constant term, $\pm 0.04 \text{ kJ} \cdot \text{mol}^{-1}$.

The following relationship of HF concentration to the enthalpy of solution (in $\text{kJ} \cdot \text{mol}^{-1}$) was obtained for a least squares fit of the data from the 14 experiments near 298.15 K and using $\sim 1 \text{ g}$ of BeO (Nos. 1, 4, 5, 6, 7, 8, 9, 14, 15, 16, 20, 22, 23, and 24) given in tables 1 and 2:

$$\Delta H \text{ at } 298.15 \text{ K} = -101.30^* - 0.0999 (\text{wt\% HF} - 24) + 0.00659 (\text{wt\% HF} - 24)^2.$$

The standard error of the estimate of ΔH is $\pm 0.12 \text{ kJ} \cdot \text{mol}^{-1}$ and the standard errors of the constants are ± 0.05 , ± 0.0071 , and ± 0.00114 , respectively.

*These values have been increased by 0.22 percent to correct for the BeSO_4 impurity in the sample as described at the end of this section.

TABLE 2. Calorimetric data for solutions of BeO(c) in HF(aq)

Expt. No.	Sample mass	EEE_i	EEE_f	Duration of reaction	Stirring energy corr.	ΔR_c	\bar{T} reaction		$-\Delta H(T)$
							$^{\circ}\text{C}$	K	
	<i>g</i>	$\text{J} \cdot \Omega^{-1}$	$\text{J} \cdot \Omega^{-1}$	<i>min</i>	Ω	Ω			$\text{kJ} \cdot \text{mol}^{-1}$
1	1.00461	15,122.50	15,211.98	215	0.005659	0.267329	26.104	299.254	100.948
2	0.99896	15,709.97	15,809.88	190	.004376	.255894	29.570	302.720	100.973
3	.98164	15,688.63	15,788.83	190	.004158	.251187	29.568	302.718	100.729
4	.98010	15,598.57	15,705.42	220	.004640	.253170	24.743	297.893	101.124
5	.88115	15,590.07	15,692.21	310	.004437	.227897	24.692	297.842	101.181
6	.99350	15,924.52	16,025.89	230	.003311	.250232	25.774	298.924	100.638
7	1.01669	15,887.56	15,988.11	230	.003235	.256641	25.051	298.201	100.626
8	1.01819	15,884.66	15,986.85	230	.003458	.256922	25.050	298.200	100.574
9	0.99474	15,605.42	15,710.15	230	.003443	.256228	25.138	298.288	100.876
10	1.00159	15,696.68	15,793.16	200	.002988	.256612	30.043	303.193	100.895
11	0.33178	15,775.32	15,805.51	190	.004294	.084414	20.115	293.265	100.485
12	.32602	15,775.66	15,808.84	190	.003419	.082964	20.084	293.234	100.515
13	.33549	15,777.37	15,812.70	190	.003907	.084978	20.073	293.223	100.066
14	.99788	16,389.99	16,469.80	435	.007083	.241164	24.298	297.448	99.314
15	.96894	16,390.14	16,469.51	405	.005916	.234906	24.253	297.403	99.626
16	.98760	16,396.71	16,476.73	265	.004225	.238649	24.287	297.437	99.342
17	.30206	15,880.24	15,911.89	195	.003203	.076619	25.426	298.576	100.850
18	.31418	15,883.10	15,908.92	195	.003604	.079494	25.447	298.597	100.597
19	.30770	15,891.29	15,897.92	130	*.011244	.077442	25.496	298.646	100.055
20	1.02937	15,171.25	15,274.16	180	.003963	.274283	25.299	298.449	101.452
22	0.98844	15,169.02	15,270.48	190	.003964	.263342	24.814	297.964	101.419
23	1.02572	15,173.78	15,274.59	180	.003512	.273448	24.868	298.018	101.513
24	1.02517	15,171.86	15,274.00	185	.003936	.273145	24.941	298.091	101.446
25	1.01137	15,970.75	16,067.96	100	.001508	.254713	41.959	315.109	100.908
26	0.96183	15,949.98	16,033.49	120	.002302	.242418	41.872	315.022	100.810
27	.99963	15,858.45	15,949.34	125	.002139	.253236	38.000	311.150	100.770
28	1.02973	16,088.96	16,171.92	65	.001173	.257031	51.885	325.035	100.705
29	0.82687	16,080.54	16,157.78	65	.001160	.206371	51.664	324.814	100.622
30	1.01751	16,082.92	16,167.87	65	.000932	.253897	51.880	325.030	100.640

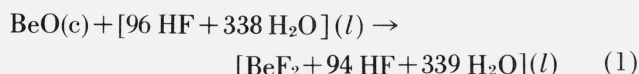
*Stirring rate changed from 250 rpm to 550 rpm.

Using a multivariable treatment of the data,⁶ a least squares fit for the data in all 29 experiments resulted in the following equation (in $\text{kJ} \cdot \text{mol}^{-1}$ and K):

$$\Delta H = -101.21^* + 0.0125 (T - 298.15 \text{ K}) \\ - 0.1066 (\text{wt\% HF} - 24) + 0.0049 (\text{wt\%} - 24)^2$$

The residual standard deviation of ΔH is $\pm 0.18 \text{ kJ} \cdot \text{mol}^{-1}$, and the standard deviations of the four coefficients are 0.05, 0.0040, 0.0095, and 0.0015, respectively. The agreement with the two equations above is good.

The seven experiments which were near 298 K and 24 percent HF given in table 3 are corrected to 298.15 K and 24 percent HF and correspond to the following equation:



$$\Delta H \text{ at } 298.15 \text{ K} = -101.30 \pm 0.20 \text{ kJ} \cdot \text{mol}^{-1} \\ = -24.21 \pm 0.05 \text{ kcal} \cdot \text{mol}^{-1}.$$

A correction of 0.22 percent was added to the mean enthalpy value given in table 3 for the SO_3 impurity in the sample (see sec. 2.1) which is probably present as BeSO_4 . The correction is based on Bear and Turnbull's value for the enthalpy of solution of BeSO_4 in HF(aq) , $-24.05 \pm 0.30 \text{ kcal/mol}$ [5]. The weight loss on drying the sample, presumably H_2O , was not a source of error because of the initial heating of the calorimetric samples. The maximum error resulting from the presence of oxides or sulfates of the metallic elements found in the spectroscopic analysis was about 0.1 percent, and twice the standard deviation of the mean of the experimental values is 0.09 percent. Therefore, an uncertainty limit of 0.2 percent was assigned to the enthalpy value in eq (1).

TABLE 3. Enthalpy of solution of BeO(c) in 24 percent HF(aq) at 298.15 K

Expt. No.	Corr. to 298.15 K	Corr. to 24% HF	$\Delta H(298.15 \text{ K})$ in 24% HF
	$\text{kJ} \cdot \text{mol}^{-1}$	$\text{kJ} \cdot \text{mol}^{-1}$	$\text{kJ} \cdot \text{mol}^{-1}$
1	-0.014	+0.012	-100.950
4	+0.003	+0.026	-101.095
5	+0.004	+0.026	-101.151
6	-0.010	-0.558	-101.206
7	-0.001	-0.536	-101.163
8	-0.001	-0.558	-101.133
9	-0.002	+0.012	-100.866
Mean			*-101.080
Standard deviation of the mean			± 0.047

*A correction of 0.22 percent should be added to this value for the BeSO_4 impurity in the sample.

*These values have been increased by 0.22 percent to correct for the BeSO_4 impurity in the sample as described at the end of this section.

*Calculated by H. H. Ku, Statistical Engineering Laboratory, Institute for Basic Standards.

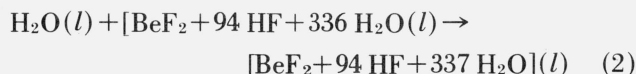
5.2. H_2O Dilution of Final Solutions of BeO(c) in HF(aq)

It is important in the correlation of data (see [1]) to have enthalpies of dilution of the final solutions. These enthalpies were measured in experiments where 0.7 g of distilled water was added to final solutions from the reactions of BeO(c) in HF(aq) . The data for these experiments are given in table 4. The electrical energy equivalents of the initial systems, EEE, were measured in each of the first four experiments, and an estimated value was used for the last two experiments. The enthalpies derived from these electrical energy equivalents refer to the final rather than the mean temperature of reaction, however the difference is negligible here.

The initial solution for the first experiment was 316.7 g of the final solution (approximately 30% HF) from Expt. No. 24 in the BeO(c) in HF(aq) series. The initial solutions for the last five experiments were each 317 g of a mixture of the final solutions (approximately 24% HF) from Expt. Nos. 25 through 30.

From the average \bar{T} react and $\Delta H(T)$ from Expt. Nos. 5 and 6 and for Expt. Nos. 2, 3, and 4 (table 4) we calculate a ΔC_p for the reaction of $\text{H}_2\text{O}(l)$ in the 24 percent HF solutions of $-1.4 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ or $-0.34 \text{ cal} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$, between 298 and 323 K.

When the enthalpies of reaction for Expt. Nos. 2, 3, and 4 are corrected to 298 K we obtain an average value for reaction (2):



$$\Delta H \text{ at } 298.15 \text{ K} = -0.334 \pm 0.020 \text{ kJ} \cdot \text{mol}^{-1} \\ = -0.080 \pm 0.005 \text{ kcal} \cdot \text{mol}^{-1}$$

The average deviation from the mean of the three experiments was $\pm 13. \text{ J} \cdot \text{mol}^{-1}$, but the larger overall uncertainty was arbitrarily assigned because of the small number of experiments and the very small temperature rise.

The value for Expt. No. 1 in 30 percent HF was $\Delta H(298.15 \text{ K}) = -0.670 \text{ kJ} \cdot \text{mol}^{-1}$ or $-0.160 \text{ kcal} \cdot \text{mol}^{-1}$.

5.3. Solution of BeO(c) in HCl(aq)

In tables 5 and 6 are the data for 11 experiments in which the enthalpy of solution of crystalline beryllium oxide in aqueous hydrochloric acid was measured. The measurements were made in 22.6 percent HCl from 347 K to 362 K, and in 18 percent HCl at 362 K.

In preliminary experiments the reaction was not complete (more than 1% of undissolved sample) after 8 h with stirring at 550 rpm in 18 percent HCl at 358 K. The first experiment of the series reported here showed that the reaction was complete in 18 percent HCl after approximately 20 h with continuous stirring at 350 rpm. Although the completeness of reaction was satisfactory the stirring energy for the long period

TABLE 4. Data for H₂O dilution experiments in BeO-HF(aq) solution

Expt. No.	H ₂ O sample mass	EEE	Stirring energy corr.	ΔR_c	Approx. HF conc.	\bar{T} reaction		$-\Delta H(T)$
	<i>g</i>	$J \cdot \Omega^{-1}$	Ω	Ω	<i>wt %</i>	$^{\circ}\text{C}$	<i>K</i>	$J \cdot \text{mol}^{-1}$
1	0.68925	15,213	0.000613	0.001686	30	24.96	298.11	670.4
2	.68728	15,657	.000634	.000824	24	24.74	297.89	338.1
3	.69654	15,668	.000702	.000775	24	24.62	297.77	313.9
4	.70544	15,651	.000701	.000872	24	24.61	297.76	348.7
5	.70078	*(16,100)	.000402	.000881	24	49.95	323.10	364.6
6	.69473	*(16,100)	.000294	.000894	24	49.95	323.10	373.2

*Estimated, not measured.

TABLE 5. Composition of reactants in the calorimetric systems for solutions of BeO(c) in HCl(aq)

Expt. No.	Initial composition			Concentration of HCl solns.		Mass of HCl soln.
	BeO	HCl	H ₂ O			
	<i>mol</i>	<i>mol</i>	<i>mol</i>	<i>mol \cdot dm^{-3}</i>	<i>wt %</i>	<i>g</i>
1	0.040119	1.568	14.444	5.375	18.01	317.37
3	.040519	1.543	14.218	5.375	18.01	312.41
4	.032737	1.493	13.755	5.375	18.01	302.24
5	.039980	1.906	13.206	6.874	22.61	307.42
6	.039615	1.906	13.206	6.874	22.61	307.42
7	.039344	1.909	13.224	6.874	22.61	307.83
8	.040995	1.907	13.207	6.874	22.61	307.44
9	.039431	1.906	13.204	6.874	22.61	307.37
10	.039862	1.907	13.207	6.874	22.61	307.45
11	.039492	1.902	13.226	6.852	22.54	307.61
12	.040870	1.902	13.228	6.852	22.54	307.64

TABLE 6. Calorimetric data for solutions of BeO(c) in HCl(aq)

Expt. No.	Sample mass	Undissolved sample	EEE _i	EEE _f	Stirring energy corr.	ΔR_c	Drift corr.	\bar{T} react		$-\Delta H(T)$
	<i>g</i>	<i>g</i>	$J \cdot \Omega^{-1}$	$J \cdot \Omega^{-1}$	Ω	Ω	Ω	$^{\circ}\text{C}$	<i>K</i>	$\text{kJ} \cdot \text{mol}^{-1}$
1	1.00421	0.00077	15,168.8	15,210.2	0.01099	0.14458	—	89.348	362.498	54.740
3	1.01394	.00051	14,964.1	15,012.5	.00336	.13757	0.01032	89.159	362.309	54.706
4	0.81943	.00063	14,639.6	14,678.7	.00303	.11390	.00835	89.121	362.271	54.742
5	1.00179	.00183	14,341.6	14,393.0	.00249	.14437	.00600	89.303	362.453	54.037
6	0.99084	—	14,194.8	14,245.2	.00304	.14595	.00575	79.648	352.798	54.453
7	.99957	.01551	14,122.5	14,158.0	.00296	.14829	*.00365	74.320	347.470	54.607
8	1.02790	.00256	14,152.7	14,189.4	.00291	.15246	*.00396	76.307	349.457	54.071
9	0.98864	.00241	14,151.5	14,189.9	.00367	.14741	.00437	76.275	349.425	54.547
10	.99701	—	14,195.0	14,233.4	.00311	.14728	.00424	79.713	352.863	54.030
11	.98865	.00088	14,198.6	14,234.2	.00441	.14494	.00420	80.107	353.257	53.688
12	1.02341	.00118	14,187.5	14,223.2	.00327	.15180	.00377	79.748	352.898	54.072

*Drift rate calculated from equation.

of time would have resulted in a large uncertainty. It was found that the stirrer and thermometer current could be turned off about 1.5 h after initiating the reaction, and the reaction proceeded slowly without stirring; the stirrer and thermometer current were turned on again about 1.5 h before the final rating period. Thus, the stirring energy was reduced to about one-seventh of that in stirring for the full reaction period, and the uncertainty was reduced accordingly. This procedure could be used only because the calorimeter is adiabatic and has an approximately isothermal surface.

The calorimeter temperature dropped slightly during long periods of unstirred drift when there was no chemical reaction. This was apparently caused by small evaporative losses through the stirrer tube. Unfortunately, these unstirred drift rates varied somewhat from one experiment to another and it was necessary to measure the drift rate for the initial system and for the final system in each experiment, and the mean of the two drift rates was used in the correction to ΔR_c for the chemical reaction. After the first experiment, the stirrer and thermometer current were off 17.5 h during the chemical reaction

periods and the initial drift measurements, and 20 h during the final drift measurements.

The drift rates varied with the calorimeter temperature and ranged from 200 to 400 $\mu\Omega \cdot \text{h}^{-1}$. The difference between initial and final drift rates ranged from 10 to 30 $\mu\Omega \cdot \text{h}^{-1}$. The drift rates for Expt. Nos. 7 and 8 were not measured, but corrections were calculated from a linear equation obtained from a least squares fit of the drift rate and temperature data in Expt. Nos. 5, 6, 9, 10, 11, and 12.

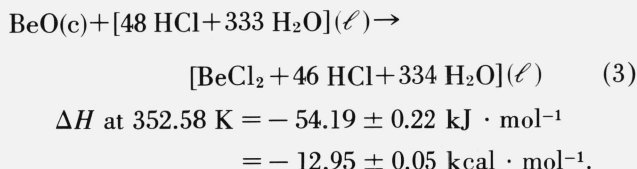
The results of Expt. No. 2 of this series were not included because the drift rates were not measured and there was insufficient data from the experiments in 18 percent HCl to calculate drift corrections.

In table 6, $\Delta H(T)$ is the enthalpy of solution at the temperature of reaction,

$$-\Delta H(T) = \frac{(25.01158)(EEE_i + EEE_f)(\Delta R_c + \text{Drift corr.})}{2(\text{Sample mass} - \text{Undissolved sample})}$$

The "Undissolved sample" was actually the insoluble residue discussed in section 2.1 except in Expt. No. 7 where the reaction was not complete at 347 K (presumably more sample would have dissolved in a longer reaction period). However, the results were used because the reaction was proceeding so slowly that the small amount of heat evolved during the final calibration was insignificant, and the calorimeter was opened immediately after the final calibration. The same procedure was followed in Expt. No. 8 at 349 K and there was no undissolved BeO. This was a good indication of the lower temperature limit for this reaction for complete solution in a reasonable length of time.

The following equation corresponds to the average value for the enthalpy of solution in 22.6 percent HCl for Expt. Nos. 5 through 12 given in table 6.



The uncertainty is twice the standard deviation of the mean of the experimental values. A correction for the SO_3 impurity in the BeO(c) was estimated to be less than 0.2 percent and was based on data for the enthalpies of formation of $\text{BeSO}_4(\text{c})$ and BeSO_4 in various aqueous HCl solutions [6]. This correction was not applied to the enthalpy value in equation (3) since it was small, uncertain, and well within the experimental uncertainty.

It was apparent from the experiments in table 6 that the ΔC_p for the reaction was small but the temperature range of the measurements was not sufficient to justify an extrapolation to 298 K. A value of ΔC_p for correcting the measured enthalpy of solution to 298 K was obtained from preliminary experiments in which electrical calibrations of the initial systems were made over the range of 298 K to 358 K and similar calibrations of the final systems were made over the same temperature range. The data are given in table 7. The Calib. No. indicates P for preliminary series and I for series I, the experiment no., and a letter for the electrical calibration, i.e., P-4b corresponds to a preliminary series, experiment no. 4, and the second electrical

TABLE 7. Electrical calibration data from which ΔC_p for the reaction of BeO(c) in HCl(aq) was obtained

Initial systems			Final systems		
Calib. No.	EEE _i	\bar{T}	Calib. No.	EEE _f	\bar{T}
	$J \cdot ^\circ\text{C}^{-1}$	$^\circ\text{C}$		$J \cdot ^\circ\text{C}^{-1}$	$^\circ\text{C}$
P-4a	1480.416	66.5852	P-4d	1495.879	86.1536
4b	1481.343	67.7193	4e	1496.646	87.2714
4c	1482.621	68.8526	4f	1497.893	88.3897
			4g	1439.480	24.7156
I-1a	1438.757	24.7999	4i	1440.981	27.1328
1b	1440.981	25.9647	4j	1455.042	40.5510
1c	1471.129	54.5756	4k	1456.187	41.7084
1d	1470.605	55.7152	4l	1457.813	42.8631
1e	1497.052	84.5474	4m	1469.360	55.1328
			4n	1469.966	56.2840
I-2a	1497.360	84.5705	4p	1481.379	69.5224
			4q	1483.103	70.6512
I-3a	1497.090	84.5573	4r	1484.511	71.7776
			4s	1495.152	84.5557
I-4a	1439.499	24.7450	4t	1495.904	85.6762
4b	1440.666	25.9212			
4c	1495.660	84.5768	I-1g	1441.472	24.8196
I-5a	1439.197	24.7129	1h	1470.806	54.5654
5b	1438.877	25.8833	1i	1497.772	84.5620
5c	1496.842	84.5628			
I-6a	1495.070	84.6242			
I-7a	1496.248	84.5620			

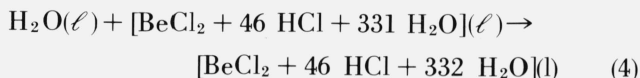
calibration of the system. A least squares fit of the data resulted in the following equations (in °C and J · °C⁻¹): EEE_i at $(T) = 1411.22 + 1.180(T) - 0.00202(T)^2$, and EEE_f at $(T) = 1413.24 + 1.108(T) - 0.00166(T)^2$. The standard error of the estimate for the first equation is $\pm 0.78 \text{ J} \cdot ^\circ\text{C}^{-1}$ and for the second equation $\pm 1.04 \text{ J} \cdot ^\circ\text{C}^{-1}$. Integrating the two equations between the limits of 25 and 79.43 °C we obtain a difference of -31 J which corresponds to an average of 0.0266 mol BeO(c) in 317 g of 18 percent HCl solution, or $\Delta(H_{352.58\text{K}} - H_{298.15\text{K}}) = -1.2 \pm 2.0 \text{ kJ} \cdot \text{mol}^{-1}$ or $-0.28 \pm 0.48 \text{ kcal} \cdot \text{mol}^{-1}$. The large uncertainty is partly the result of evaporative losses at the high temperatures. Heat capacity data for aqueous HCl solutions are not available at the temperatures and concentrations of our measurements, however, we assume from the data given by Parker [7] that the corrections obtained in 18 percent HCl solutions would be the same in 22.6 percent HCl solutions within the uncertainty given. When the correction is added to eq (3), $\Delta H(298.15 \text{ K}) = -53.0 \pm 2.0 \text{ kJ} \cdot \text{mol}^{-1}$ or $-12.67 \pm 0.48 \text{ kcal} \cdot \text{mol}^{-1}$.

From Expt. Nos. 1, 3, and 4 (table 6) we obtain a value of $\Delta H(362.4 \text{ K}) = -54.73 \text{ kJ} \cdot \text{mol}^{-1}$ or -13.08

$\text{kcal} \cdot \text{mol}^{-1}$ for the enthalpy of solution of BeO(c) in 18 percent HCl. The average deviation of the three experiments was ± 0.027 percent.

5.4. H₂O Dilution of Final Solutions of BeO(c) in HCl(aq)

The enthalpy of dilution of the final solution was measured when 0.7 g of water was added to a mixture of the final solutions of Expt. Nos. 11 and 12 (tables 5 and 6). The data for the two experiments are given in table 8. The electrical energy equivalents, EEE , were measured for only the initial systems. Therefore, the enthalpies refer to the final rather than the mean temperature of reaction; however, the difference is negligible here. The following equation corresponds to the average for the two experiments:



$$\begin{aligned} \Delta H \text{ at } 298.15 \text{ K} &= -1.14 \text{ kJ} \cdot \text{mol}^{-1} \\ &= -0.27 \text{ kcal} \cdot \text{mol}^{-1}. \end{aligned}$$

TABLE 8. Data for H₂O dilution in final solutions of BeO-HCl(aq)

Expt. No.	Wt. of calor. soln. (in air)	H ₂ O sample mass	EEE	Stirring energy corr.	ΔR_c	\bar{T} reaction		$-\Delta H(T)$
						°C	K	
	g	g	$\text{J} \cdot \Omega^{-1}$	Ω	Ω			$\text{J} \cdot \text{mol}^{-1}$
1	297.18	0.70431	13,147.	0.001168	0.003351	25.09	298.24	1127.
2	269.68	.72752	12,353.	.000755	.003756	25.09	298.24	1149.
Mean of 2 = 1138. $\text{J} \cdot \text{mol}^{-1}$ or 272.0 $\text{cal} \cdot \text{mol}^{-1}$								

6. Conclusions

Kolesov, et al., measured the enthalpy of reaction of BeO(c) in 22.6 percent HF(aq) at 21 °C as $-24.17 \pm 0.12 \text{ kcal} \cdot \text{mol}^{-1}$ [8]. This value corrected for temperature and acid concentration using our equations in section 5.1 is $\Delta H(298.15 \text{ K}) = -24.19 \text{ kcal} \cdot \text{mol}^{-1}$ which is in good agreement with our value, $-24.21 \pm 0.05 \text{ kcal} \cdot \text{mol}^{-1}$, given in eq (1). No values have been reported previously for the enthalpy of reaction of BeO(c) in aqueous HCl.

The values for the enthalpies of solution of BeO(c) in HF(aq) and in HCl(aq) as well as the temperature and dilution effects reported here were used with comparable enthalpies of solution of Be(c) and the enthalpy of formation of H₂O(l) to obtain values for the enthalpy of formation of BeO(c). These results are discussed in detail in the paper by V. B. Parker which follows this.

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